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PATENT ABSTRACTS OF JAPAN

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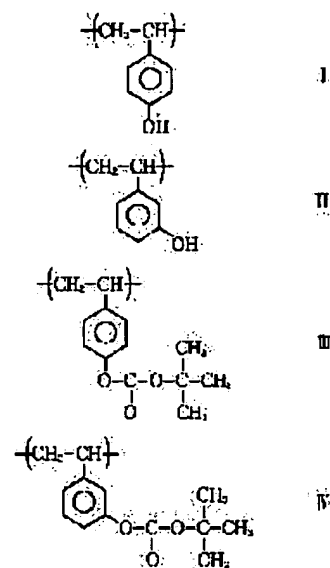
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YAMADA MOTOYUKI

(54) P-HYDROXYSTYRENE/M-HYDROXYSTYRENE BLOCK COPOLYMER PARTIALLY ESTERIFIED WITH TERT-BUTOXYCARBONYL GROUP AND ITS PRODUCTION

(57)Abstract:

PURPOSE: To obtain a polymer of high developability and high resolution by esterifying part of the hydroxyl groups of a specified part of a specified p-hydroxystyrene/m-hydroxystyrene block copolymer with tert-butoxycarbonyl groups.

CONSTITUTION: Part of the hydroxyl groups of the poly-p-hydroxy-styrene part and the poly-m-hydroxystyrene part of a monodisperse p-hydroxystyrene/m-hydroxystyrene block copolymer having a weight-average molecular weight to number-average molecular weight ratio of 1.01-1.5 are esterified with tert-butoxycarbonyl groups to obtain a partially esterified p-hydroxystyrene/m-hydroxystyrene block copolymer comprising repeating units of formulas I, II, III and IV. The obtained copolymer can easily be developed with an alkali and has a narrow molecular weight distribution and therefore can desirably be used as e.g. a resist material for LSI.



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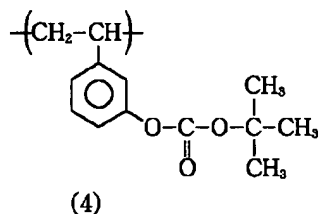
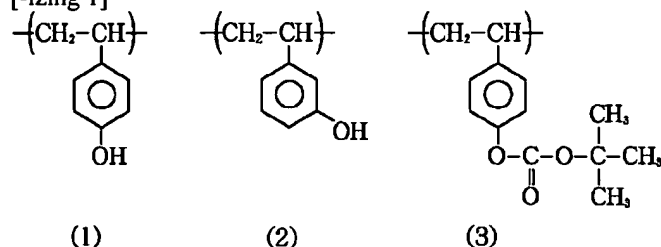
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CLAIMS

[Claim]

[Claim 1] The p-hydroxy styrene-m-hydroxy styrene block copolymer by which partial esterification of the hydroxyl group of the poly (p-hydroxy styrene) section which has the repeat unit shown by the following structure expression (1), (2), (3), and (4), and is characterized by molecular weight distributions being weight-average-molecular-weight (Mw) / number-average-molecular-weight (Mn) = 1.01-1.5, and the poly (m-hydroxy styrene) section was carried out by the tert-butoxy carbonyl group.

[izing 1]



[Claim 2] The manufacture technique of the p-hydroxy styrene-m-hydroxy styrene block copolymer claim 1 publication that weight-average-molecular-weight (Mw) / number average molecular weight (Mn) carries out the tert-butoxy carbonylation of the hydroxyl group of the poly (p-hydroxy styrene) section in the block copolymer of the p-hydroxy styrene of the mono dispersion nature of 1.01-1.5, and m-hydroxy styrene, and the poly (m-hydroxy styrene) section partially.

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DETAILED DESCRIPTION

[Detailed description]

[0001]

[Field of the Invention] this invention relates to the p-hydroxy styrene-m-hydroxy styrene block copolymer and its manufacture technique of the mono dispersion nature by which partial esterification of the hydroxyl group of the poly (p-hydroxy styrene) section suitably used as resist material for LSI etc. and the poly (m-hydroxy styrene) section was carried out by the tert-butoxy carbonyl group.

[0002]

[A Prior art and Object of the Invention] Conventionally, as a base polymer for resist materials used as the object for the lithography of a high resolution, or an object for LSI, the functional polymer is used abundantly. In connection with the development of high-density-izing especially in LSI in recent years, a high resolution and high development nature come to be increasingly demanded about a resist material, and although the novolak resin was conventionally used in use as a functional polymer which can meet such a demand, the chemistry amplification type resist material is variously examined as what is replaced with this in recently.

[0003] Especially in the resist material above-mentioned chemistry amplification type, while it has the functional group easily desorbed with an acid from the viewpoint of workability, the object for prizes of that from which the solubility in the desorption order of the functional group is different is carried out. The polystyrene derivative which is excellent in plasma-proof nature as such a resist material is especially known as a suitable thing.

[0004] Although the molecular weight and molecular weight distribution have big influence on the development property and resolution of a resist in using these polymers as a base polymer for resists, these polymers are polydispersed polymers obtained by a usual radical polymerization method and a usual condensation-polymerization method, and since they are not considered [controlling molecular weight and molecular weight distribution from the start, and], in order to raise the development nature and resolution of a resist, they are controlling molecular weight using the technique of fractionation.

[0005] However, since the technique of fractionation was difficult to fully follow in footsteps to the demand performance which becomes severe for operation to be not only complicated, but when there is a fault of taking time, it was what cannot become the essential means of a problem solving.

[0006] Therefore, the development of a quality polymer suitable as a base polymer for resist materials was desired.

[0007] Since it has the functional group which it was made in order that this invention might meet the above-mentioned request, and is easily desorbed with an acid While negatives can be easily developed with alkali by the solubility in the desorption order of the functional group differing It has high development nature and a high resolution. As a resist material etc. The p-hydroxy styrene-m-hydroxy styrene block copolymer by which partial esterification of the hydroxyl group of the useful poly (p-hydroxy styrene) section and the poly (m-hydroxy styrene) section was carried out by the tert-butoxy carbonyl group, and its manufacture technique It aims at providing.

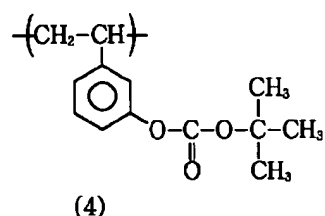
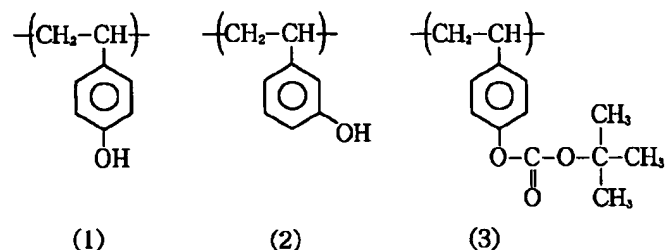
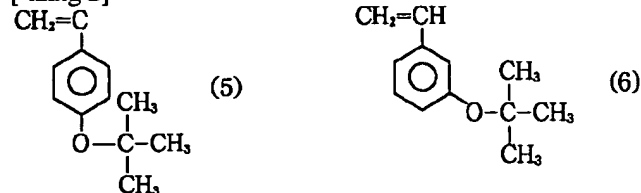
[0008]

[A The means for solving a technical problem and an operation] After carrying out the living polymerization of the m-tert-butoxy styrene shown with the p-tert-butoxy styrene shown with the following structure expression (5), and the following structure expression (6) as a result of repeating a study zealously, in order that this invention person may attain the above-mentioned purpose, By making tert-butyl in a molecule desorb, the block copolymer of the p-hydroxy styrene of the mono dispersion nature of 1.01-1.5 and m-hydroxy styrene is obtained for weight-average-molecular-weight (Mw) / number average molecular weight (Mn), And by carrying out the tert-butoxy carbonylation of the hydroxyl group of the poly (p-hydroxy styrene) section in this block copolymer, and the poly (m-hydroxy styrene) section partially It has the repeat unit shown by the following structure expression (1), (2), (3), and (4). And poly whose molecular weight distribution are Mw/Mn=1.01-1.5 The block copolymer of the p-hydroxy styrene and m-hydroxy styrene by which partial esterification of the hydroxyl group of the section and the poly (m-hydroxy styrene) section was carried out by the tert-butoxy carbonyl group, respectively is obtained, (p-hydroxy styrene) While a control of molecular weight gives the block copolymer of the mono dispersion nature of Mw/Mn=1.01-1.5 certainly easily, this technique Thus, it has the tert-butoxy carbonyl group which the obtained mono dispersion nature block copolymer may desorb easily with an acid. When negatives were able to be easily developed with alkali, even if it did not perform troublesome technique of fractionation by mono dispersion nature, it had high development nature and the high resolution, and the knowledge of the ability to use suitable for intended use, such as a

base polymer for resist materials, as a functional polymer so is carried out, and it came to make this invention.

[0009]

[-izing 2]

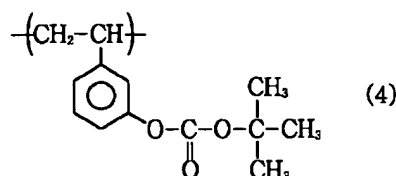
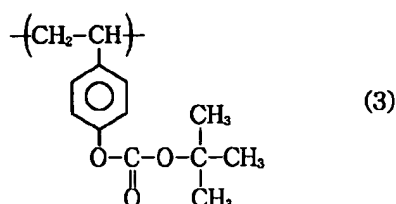
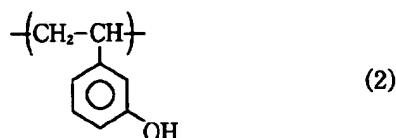
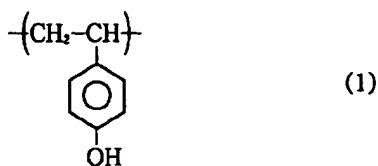


[0010] Therefore, this invention has the repeat unit shown by the above-mentioned structure expression (1), (2), (3), and (4). Molecular weight distribution And weight average molecular weight (Mw) /number average molecular weight (Mn) The p-hydroxy styrene-m-hydroxy styrene block copolymer by which partial esterification of the hydroxyl group of the poly (p-hydroxy styrene) section characterized by being =1.01-1.5 and the poly (m-hydroxy styrene) section was carried out by the tert-butoxy carbonyl group, Weight-average-molecular-weight (Mw) / number average molecular weight (Mn) and the hydroxyl group of the poly (p-hydroxy styrene) section in the block copolymer of the p-hydroxy styrene of the mono dispersion nature of 1.01-1.5, and m-hydroxy styrene, and the poly (m-hydroxy styrene) section The manufacture technique of the block copolymer with the p-hydroxy styrene-m-hydroxy styrene which carries out a tert-butoxy carbonylation partially and by which partial esterification was carried out [above-mentioned] is offered.

[0011] Hereafter, partial esterification of the hydroxyl group of the poly (p-hydroxy styrene) section which has per this invention and also the repeat unit the block copolymer of this invention is indicated to be by the following structure expression (1), (2), (3), and (4) when it explains in full detail, and the poly (m-hydroxy styrene) section is carried out by the tert-butoxy carbonyl group.

[0012]

[-izing 3]



[0013] Although the repeat unit of the above-mentioned formula (1), (2), (3), and (4) may be contained at an arbitrary rate, here Usually, it is desirable to contain at a rate from which a weight fraction is set to $0.01 \leq (1) \leq 99.97$, $0.01 \leq (2) \leq 99.97$, $0.01 \leq (3) \leq 99.97$, $0.01 \leq (4) \leq 99.97$, and $(1)+(2)+(3)+(4)=1$. When using especially the block copolymer of this invention as resist material The soluble difference at the time of the development of a resist From the viewpoint of a crosslinking reaction control to and $20 \leq (1) \leq 99.98$, $0.01 \leq (2) \leq 50$, $0.01 \leq (3) \leq 80$, $0.01 \leq (4) \leq 50$, and to be more preferably referred to as $50 \leq (1) \leq 99.8$, $0.01 \leq (2) \leq 20$, $0.01 \leq (3) \leq 45$, and $0.01 \leq (4) \leq 20$.

[0014] furthermore, as for especially the rate of the partial esterification by the t-butoxycarbonyl machine of the hydroxyl group in a molecule, in the above-mentioned block copolymer, it is desirable that it is 5 - 45% 0.1 to 80% (weight % and the following -- the same) to poly (p, m-hydroxy styrene)

[0015] The block copolymer of the above-mentioned p-hydroxy styrene of this invention and m-hydroxy styrene is the thing of the mono dispersion nature to which Mw/Mn has 1.01-1.5, and molecular weight distribution that serve as the domain of 1.01-1.3 preferably. If that with which Mn does not fill Mw/1.01 is technically difficult to compound and 1.5 is exceeded, it cannot obtain the high resolution of the grade which can be used as a resist material, and the degree of high development. In addition, weight average molecular weight (Mw) can measure number average molecular weight (Mn) again by the light scattering measurement using a membrane osmometer.

[0016] Furthermore, when using it as a resist material, generally the domain of 500-500,000 and that it is especially the domain of 3,000-300,000 have number average molecular weight desirable although especially the average molecular weight of the above-mentioned block copolymer is not restricted. When number average molecular weight may not have a layer intensity and exceeds 500,000 as a resist material less than by 500, a problem is in a development property and a compatibility, and a high resolution and the degree of high development may be unable to be obtained.

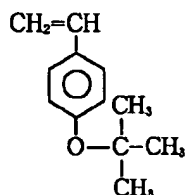
[0017] In addition, a gel permeation chromatography (GPC) can perform evaluation of the above-mentioned molecular weight distribution, and the molecular structure can be easily checked by the ¹H-NMR spectrum.

[0018] The partial esterification p-hydroxy styrene-m-hydroxy styrene block copolymer of the mono dispersion nature mentioned above in this invention can be easily obtained by esterifying partially the hydroxyl group of a mono dispersion nature p-hydroxy styrene-m-hydroxy styrene block copolymer with a t-butoxycarbonyl machine, as shown below.

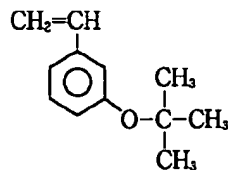
[0019] First, the block copolymer of the p-hydroxy styrene of mono dispersion nature and m-hydroxy styrene can be obtained by desorbing t-butyl in a molecule here, after carrying out the living polymerization of both the monomers of the m-t-butoxy styrene shown with the p-t-butoxy styrene shown with the following structure expression (5), and the following structure expression (6).

[0020]

[-izing 4]



(5)



(6)

[0021] Moreover, it is desirable to use an organometallic compound as a polymerization initiator in case of the living polymerization of the above-mentioned monomer. As an organometallic compound, organic alkali metal, such as n-butyl lithium, sec-butyl lithium, t-butyl lithium, sodium naphthalene, anthracene sodium, alpha-methyl-styrene tetramer disodium, a cumyl potassium, and cumyl caesium, etc. is mentioned, for example. In addition, it is dependent on the molecular weight of the polymer to generate, and the addition of a polymerization initiator is computed from molecular weight and the weight of a monomer (the number of mols of the weight/initiator of a molecular weight = monomer).

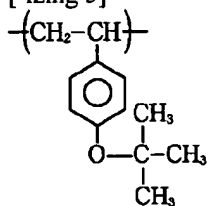
[0022] As for a living polymerization, it is desirable to carry out in an organic solvent generally. As an organic solvent, an aromatic hydrocarbon, cyclic ether, an aliphatic hydrocarbon solvent, etc. are illustrated, and benzene, toluene, a tetrahydrofuran, a dioxane, a tetrahydropyran, dimethoxyethane, n-hexane, a cyclohexane, etc. are mentioned as an example. Even if it uses it independently, you may use these organic solvents combining two or more sorts, respectively. In addition, as for especially the concentration in the organic solvent of both the above-mentioned monomers formula (5) and (6), considering as 1 - 30% is desirable one to 50%.

[0023] It is desirable to agitate a reaction under a high vacuum or the inert gas ambient atmosphere, such as an argon and nitrogen, and to perform it. Although reaction temperature can be chosen freely in between to the boiling point temperature of the organic solvent used from -100 degrees C, it is desirable to make it especially react at a room temperature by the tetrahydrofuran solvent by -78 degrees C - 0 degree C and the benzene solvent. Moreover, it is suitable to usually perform a reaction for about 10 minutes to 20 hours.

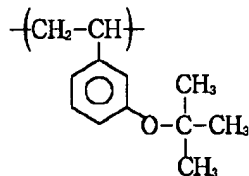
[0024] A halt of a reaction is performed by adding halt agents, such as a methanol, water, and a methyl star's picture, to the system of reaction. Subsequently, the obtained reaction mixed solution is made to precipitate in a suitable solvent, for example, a methanol, and by washing and drying, the polymer generated by the polymerization reaction can be refined and it can isolate. In addition, if a living-polymerization reaction is performed in this way, only the vinyl group in the above-mentioned formula (5) and the monomer of (6) will react alternatively, and will carry out a polymerization, and the block copolymer which has the repeat unit shown by the following structure expression (7) and (8) will be obtained.

[0025]

[-izing 5]



(7)



(8)

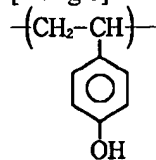
[0026] Thus, the molecular weight distributions Mw/Mn of the copolymer obtained are the things of the mono dispersion nature of 1.01-1.5.

[0027] In addition, since the yield of the polymer in the above-mentioned reaction is about 100%, the molecular weight of the polymer obtained is easily computable from the weight of the used monomer, and the number (molecularity) of mols of a polymerization initiator.

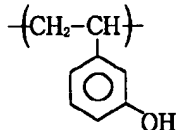
[0028] Next, if t-butyl in the block copolymer which has the repeat unit shown by the above-mentioned formula (7) and (8) is made to desorb, the block copolymer of the p-hydroxy styrene and m-hydroxy styrene which have the phenol residue structural unit shown by the following structure expression (9) and (10) by things will be obtained.

[0029]

[-izing 6]



(9)



(10)

[0030] The elimination reaction of the above-mentioned t-butyl can be performed [drop / acids, such as a hydrochloric acid

and a hydrobromic acid, / in a mixed solvent / independent or /, such as a dioxane, an acetone, an acetonitrile, and benzene,] easily. In these reactions, since it does not say that the principal chain of a macromolecule is cut or crosslinking reaction happens between molecules, the molecular weight distribution of the block copolymer of the p-t-butoxy styrene and m-t-butoxy styrene which are a precursor are maintained as it is, and the block copolymer of the p-hydroxy styrene of mono dispersion with narrow molecular weight distribution and m-hydroxy styrene can be obtained.

[0031] In addition, what is necessary is just to add the addition of an acid more than mols [poly / poly (p-hydroxy styrene), / (m-hydroxy styrene)] in this case.

[0032] Furthermore, the reaction which t-butoxycarbonyl-izes partially the hydroxyl group of the poly (p-hydroxy styrene) section of the block copolymer of the above-mentioned p-hydroxy styrene of mono dispersion and m-hydroxy styrene and the poly (m-hydroxy styrene) section can be easily performed like a usual t-butoxycarbonyl-ized reaction.

[0033] As a t-butoxycarbonyl-ized reagent, for example, ***** acid-t-butyl, G t-butyl carbonate, t-butoxycarbonyl thio - (4, 6-dimethyl pyridine), t-butyl pentachlorophenyl carbonate, 2-(t-*****)-2-phenylacetonitrile, etc. are used. And the hydroxyl group of the poly (p-hydroxy styrene) section of mono dispersion and the poly (m-hydroxy styrene) section is t-butoxycarbonyl-ized partially, using a pyridine, a tetraethyl amine, etc. as an acid trap solvent. In this case, you may add to the system of reaction, using dimethylamine, 4-N, and N-dimethylamino pyridine etc. as a t-butoxycarbonyl-ized catalyst if needed. In addition, the amount of the t-butoxycarbonyl-ized reagent used is the amount of proportionalities at the rate of t-butoxycarbonyl-izing, and let the addition of a t-butoxycarbonyl-ized catalyst be the amount of catalysts. Furthermore, mols [reagent / t-butoxycarbonyl-ized] are suitable for the amount of the acid trap solvent used.

[0034] Moreover, the block copolymer of p-hydroxy styrene and m-hydroxy styrene can be made into potassium salt using potassium-t-butoxide, and the block copolymer of the p-hydroxy styrene of mono dispersion and m-hydroxy styrene can be partially t-butoxycarbonyl-ized also by the technique to which this is made to react with di-t-butylidicarbonate. In addition, the t-butoxycarbonyl-ized reaction in this invention is not limited to the above-mentioned reaction.

[0035] Thus, the rate of t-butoxycarbonyl-izing of a partial esterification mono dispersion nature p-hydroxy styrene-m-hydroxy styrene copolymer of this invention obtained It is what can be easily checked by the ¹H-NMR spectrum. this rate of t-butoxycarbonyl-izing As mentioned above, it is desirable that it is 5 - 45% of a domain especially 0.1 to 80% to the soluble difference at the time of the development of a resist and the viewpoint of a crosslinking reaction control to poly (p-hydroxy styrene) and poly (m-hydroxy styrene), respectively.

[0036]

[Effect of the invention] The p-hydroxy styrene-m-hydroxy styrene block copolymer by which partial esterification was carried out with the t-butoxycarbonyl machine of this invention can carry out alkali development, and since molecular weight distribution are narrow, it is suitable as photosensitive polymeric materials, such as a resist material of a high resolution. Moreover, according to the manufacture technique of this invention, the molecular weight can be controlled arbitrarily and easily, and the block copolymer with the p-hydroxy styrene-m-hydroxy styrene of the t-butoxycarbonyl base part ester of the above-mentioned mono dispersion nature can be manufactured advantageously industrially.

[0037]

[Example] this invention is not limited by this, although an example is shown and this invention is explained further in full detail hereafter.

[0038] [Example]

Tetrahydrofuran 2300ml was taught as a solvent, 8xten - three mols of n-butyl lithiums were taught the flask of 3l. of synthesis of the block copolymer of the p-hydroxy styrene of mono dispersion nature, and m-hydroxy styrene as an initiator, and it mixed. The reaction solution presented red the place to which the polymerization reaction was made to perform, having added p-tert-butoxy styrene 100g in this solution, having made the polymerization reaction perform, agitating for 2 hours, having added m-tert-butoxy styrene 5g next, and agitating for 2 hours, after cooling the obtained mixed solution at -78 degrees C. Subsequently, after having added the methanol in the obtained reaction solution and making it stop a polymerization reaction as a reaction halt agent, this solution is poured out into a methanol, the obtained polymer is settled, and 104g of white polymers was obtained the place which carried out separation xeransis.

[0039] The measurement result of ¹H-NMR of the obtained polymer is as follows.

1.4-2.2 ppm : (broadcloth, 3H, and -CH₂-CH-)

1.3-1.6 ppm : (broadcloth, 9H, -OC₃ (CH₃))

6-7 ppm : (broadcloth, 4H, C₆H₄)

[0040] From the ¹H-NMR measurement result, it was checked that the above-mentioned copolymer is a copolymer which consists of p-tert-butoxy styrene 95% and m-tert-butoxy styrene 5%. Moreover, when number average molecular weight was measured by the layer osmometry, it was 1.2x10⁴g/mol. Furthermore, the thing with very high (M_w/M_n=1.09) mono dispersion nature was checked from the result of GPC elution diagram. In addition, GPC elution diagram is as having been shown in drawing 1.

[0041] Subsequently, after having added the 20g of the above-mentioned copolymers to acetone 300ml and making it melt, the little concentrated hydrochloric acid was added at 60 degrees C. After agitating the obtained solution for 8 hours, this solution is poured out underwater and polymer 13g was obtained the place washed and dried.

[0042] When the number average molecular weight of this polymer was measured by the layer osmometry, it was 7600g/mol. Moreover, the result which evaluated the molecular weight distribution of this polymer by GPC is as having been shown in

drawing 2 , and it was checked that it is a copolymer with very high mono dispersion nature. Furthermore, since the peak which originates from the measurement result of ¹H-NMR of the polymer obtained here at tert-butyl was not observed, a polymer is the copolymer of poly (p-hydroxy styrene) and poly (m-hydroxy styrene), and not having tert-butyl at all was checked.

[0043] 100g (molecular weight 7600, molecular weight distribution 1.15) of the block copolymers of the p-hydroxy styrene and m-hydroxy styrene which were obtained by the synthetic above-mentioned living polymerization of the block copolymer of the p-hydroxy styrene and m-hydroxy styrene by which partial esterification was carried out by the tert-butoxy carbonyl group was melted in 1l. of pyridines, and 40g of 2 carbonic-acid G t-butyl was added, agitating at 45 degrees C. Although gas occurred simultaneously with addition, it was made to react in N₂ draft further for 1 hour. The reaction mixture was dropped at 1l. of the water containing 20g of concentrated hydrochloric acids, and white sedimentation was obtained. After filtering, acetone 50ml was made to carry out sedimentation lysis, and it was dropped at 1l. of water. Subsequently, after filtering sedimentation, the vacuum drying was carried out below 40 degrees C.

[0044] The obtained polymer was 19.6%, as a result of having the repeat unit of the aforementioned formula (1), (2), (3), and (4) and asking for the rate of an introduction of a tert-butoxy carbonyl group using the peak of 8 ppm OH base in ¹H-NMR, and molecular weight distribution were 1.15.

[Translation done.]

PTO 2003-1627

Japan Kokai

Japanese Patent Publication

Publication No.: 6-49137

P - HYDROXY STYRENE - M - HYDROXY STYRENE BLOCK COPOLYMER
ESTERIFIED PARTIALLY WITH THE TERT - BUTHOXY CARBONYL GROUP
AND ITS PRODUCTION METHOD

[Tert - butokishi karuboniru ki de bubun esuterukasareta p
hidorokishi suchiren - m hidorokishisuchiren burokku kyo jugo'tai
oyobi sono seizo hoho]
Osamu Watababe et al

UNITED STATES PATENT AND TRADEMARK OFFICE

Washington, D.C.

February 2003

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esuterukasareta p - hidorokishi suchiren
- m - hidorokishi suchiren burokku kyo
jugo'tai oyobi sono seizo hoho
English title : p - hydroxy styrene - m - hydroxy
styrene block copolymer esterified
partially with the tert - butoxy
carbonyl group and its production method

[Title of Invention] p - hydroxy styrene - m - hydroxy styrene block copolymer esterified partially with tert - butoxy carbonyl group and its production method

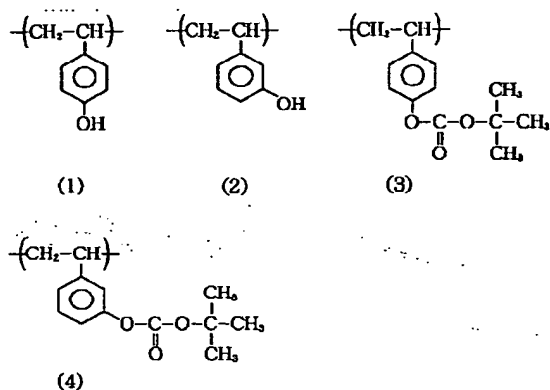
[Summary]

[Purpose] To offer a polymer suitable for use as a resist material, as a functional polymer, it has good development property and high resolution property with single dispersability and can be developed easily with an alkaline solution.

[Constitution] The hydroxide group of a part of poly (m - hydroxy styrene) and a part of poly (p - hydroxy styrene) in the block copolymer of the p - hydroxy styrene and the m - hydroxy styrene are esterified partially by tert - butoxy carbonyl, this is single dispersed having average molecular weight (Mw)/average molecular number (Mn) in the range of 1.01 - 1.5. It consists of repeated units shown by these structural formula (1)(2)(3)(4). Also, the hydroxide group of a part of poly (p - hydroxy styrene) and a part of poly (m - hydroxy styrene) is partially esterified with tert - butoxy carbonyl group, the molecular weight distribution is the average molecular weight (Mw)/ average molecular number (Mn) = 1.01 - 1.5, the p - hydroxy styrene - m - hydroxy styrene block copolymer is obtained.

¹ Numbers in the margin indicate pagination in foreign text.

[Formula 1]



/2

[Scope of Patent Claims]

[Claim 1] The hydroxide group of a part of poly (p - hydroxy styrene) and a part of poly (m - hydroxy styrene) is partially esterified with tert - butoxy carbonyl group, the molecular weight distribution is average molecular weight (Mw)/ average molecular number (Mn) = 1.01 - 1.5, p - hydroxy styrene - m - hydroxy styrene block copolymer is obtained. The repeated units are shown with the structural formula shown below (1), (2), (3) and (4).

[Claim 2] The production method of the p - hydroxy styrene - m - hydroxy styrene block copolymer of Claim 1 is characterized in that the hydroxide group of a part of poly (m - hydroxy styrene) and a part of poly (p - hydroxy styrene) in the block copolymer of the p - hydroxy styrene and the m - hydroxy styrene are esterified partially by tert - butoxy carbonyl, this is single dispersed having average molecular weight (Mw)/average molecular number (Mn) in the range of 1.01 - 1.5.

[Detailed explanation of invention]

[0001]

[Industrial field of use] The invention pertains to the production method of p- hydroxy styrene - m - hydroxy styrene block copolymer, the hydroxide group of a part of poly (p - hydroxy styrene) and a part of poly (m - hydroxy styrene) is partially esterified with tert - butoxy carbonyl group. This is suitable as a resist material for LSI.

[0002]

[Prior Art and the problems resolved by the invention] Conventionally, a functional polymer is used as the base polymer for a resist material used in LSI or for lithography of high resolution. In particular, the demand for high resolution and high development properties are high with the resist material as LSI becomes highly dense. To meet this demand, the novolak resin have been used conventionally as the functional polymer. This type of resin was used mainly for this purpose. Recently, various research were focused on the resist material of the chemical width increasing type.

[0003] For this type of resist material of chemical width increasing type, a polymer with different solubility is used for separating the functional group and the functional group can be separated easily with an acid, this type is used from the observation point of production. The polystyrene derivative that have excellent plasma resistance is most suitable as the resist material.

[0004] When this polymer is used as the polymer for the resists, the molecular weight and the molecular weight distribution have a

big influence on the development characteristics and resolution of the resist so these polymers is a multidispersed polymer obtained by the normal radical polymerization and the condensation polymerization method. Since the molecular weight and molecular distribution can be controlled, the development and resolution of the resist is improved, the control of the molecular weight can be carried out using other means.

[0005] However, the drawback is that the other means is complex and takes a long time so in order to obtain a resist with sufficient properties, the purpose of the invention is to obtain a means to resolve this problem.

[0006] Therefore, the development for a polymer of high quality as the polymer for the resist material is desired.

[0007] By focusing the invention on the above purpose, since the functional group can separate easily by an acid, right after the separation of the functional group, the development is carried out with an alkaline solution. This resist has high resolution property and high development property. The purpose of the invention is to offer a production method of p- hydroxy styrene - m - hydroxy styrene block copolymer, the hydroxide group of a part of poly (p - hydroxy styrene) and a part of poly (m - hydroxy styrene) is partially esterified with tert - butoxy carbonyl group. This is suitable as a resist material for LSI.

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[0008]

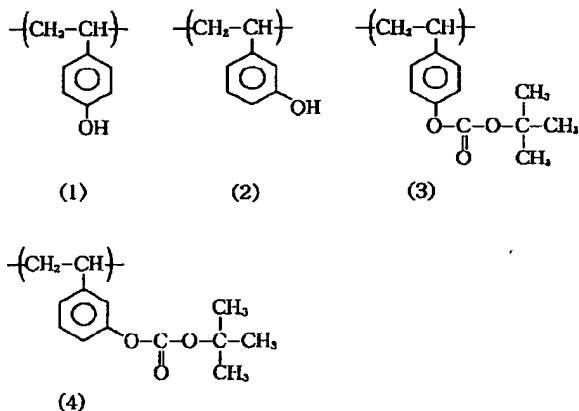
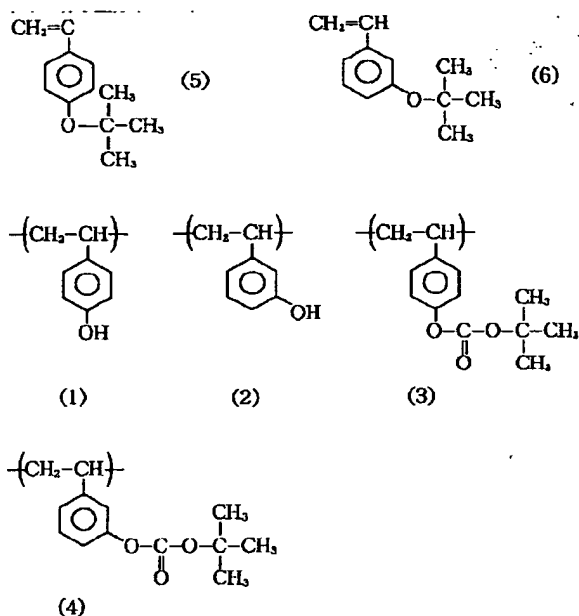
[Means and action for resolving the problem] As a result of the

inventors focusing their research on the above problem, the invention attained success. After p - tert - butoxy styrene shown with the structural formula (5) shown below and m - tert - butoxy styrene shown with the structural formula (6) shown below are living polymerized, the tert - butyl group in the polymer is separated, the block copolymer of p - hydroxy styrene and the m - hydroxy styrene of single dispersability and having an average molecular weight of (Mw)/average molecular number (Mn) of 1.01 - 1.5. Then, the hydroxide group of a part of poly (p - hydroxy styrene) and a part of poly (m - hydroxy styrene) of the said block copolymer are partially esterified with tert - butoxy carbonyl group. The repeated units are shown with the structural formula shown below, (1), (2), (3) and (4). The molecular weight distribution is the average molecular weight (Mw)/ average molecular number (Mn) = 1.01 - 1.5. The hydroxide group of a part of poly (p - hydroxy styrene) and a part of poly (m - hydroxy styrene) are partially esterified with tert - butoxy carbonyl group, a block copolymer of p - hydroxy styrene and m - hydroxy styrene is obtained. The molecular weight can be controlled with this method. The block copolymer of single dispersability of (Mw)/ (Mn) = 1.01 - 1.5. The single dispersed copolymer is separated easily by an acid, it has the tert - butoxy carbonyl group. It can be developed easily with an alkaline solution. It has high development property and high resolution without using a difficult means and it has single dispersability. It is suitable for use as the base polymer used as resist material as the functional polymer.

The invention attained success.

[0009]

[Formula 2]



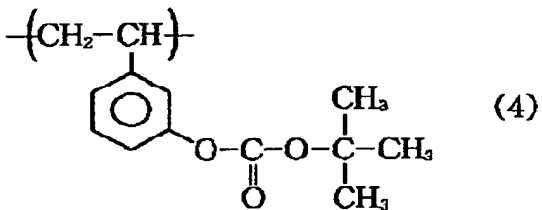
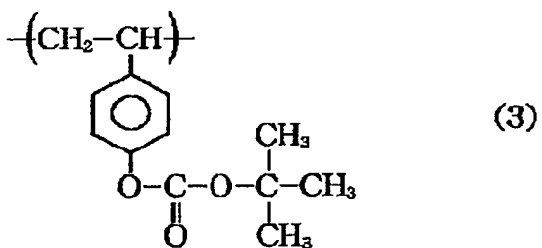
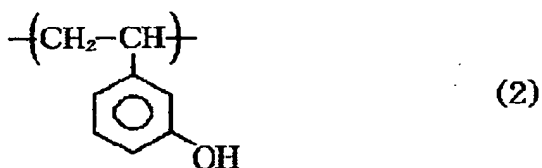
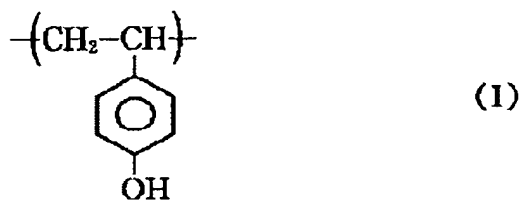
[0010] Therefore, the invention is characterized in that the repeated units are shown with the structural formula shown below, (1), (2), (3) and (4). The molecular weight distribution is the average molecular weight (M_w)/ average molecular number (M_n) = 1.01 - 1.5. The hydroxide group of a part of poly (p - hydroxy styrene) and a part of poly (m - hydroxy styrene) are partially esterified with tert - butoxy carbonyl group. P - hydroxy styrene - m - hydroxy styrene block copolymer is obtained. The molecular weight distribution is average molecular weight (M_w)/ average molecular number (M_n) = 1.01 - 1.5. The hydroxide group of a part of poly (p - hydroxy styrene) and a part of poly (m - hydroxy styrene) are partially esterified with tert - butoxy carbonyl group, a block

copolymer of p - hydroxy styrene - m - hydroxy styrene is obtained.
 [0011] To explain the invention in detail, the block copolymer of the invention have repeated units as shown with the structural formula shown below, (1), (2), (3) and (4). The hydroxide group of a part of poly (p - hydroxy styrene) and a part of poly (m - hydroxy styrene) are partially esterified with tert - butoxy carbonyl group.

/4

[0012]

[Formula 3]



[0013] Here, the repeated units of the above formula (1), (2), (3) and (4) can be any combination, it is usually this combination rate is preferred, $0.01 \leq (1) \leq 99.97$, $0.01 \leq (2) \leq 99.97$, $0.01 \leq (3) \leq 99.97$, $0.01 \leq (4) \leq 99.97$, $(1) + (2) + (3) + (4) = 1$. In particular, when the block copolymer of the invention is used as the resist material, from the observation point of the difference of solubility and the cross linking reaction control during the development of the resist, these combination rates are preferred, $20 \leq (1) \leq 99.98$, $0.01 \leq (2) \leq 50$, $0.01 \leq (3) \leq 80$, $0.01 \leq (4) \leq 50$, but most preferably $50 \leq (1) \leq 99.8$, $0.01 \leq (2) \leq 20$, $0.01 \leq (3) \leq 45$, $0.01 \leq (4) \leq 20$.

[0014] In addition, the proportion of the partial esterification by the t - butoxy carbonyl group of the hydroxide group in the molecule in the above block copolymer is in the range of 0.1 - 80 % (wt %, similar for below) to the poly (p, m - hydroxy styrene). In particular, it is preferred in the range of 5 - 45 %.

[0015] The block copolymer of the above described p - hydroxy styrene and m - hydroxy styrene have single dispersion consisting of the molecular weight distribution of M_w/M_n equals to 1.01 - 1.5 but preferably in the range of 1.01 - 1.3. When M_w/M_n is below 1.01, the synthesis is difficult technically and if it is over 1.5, the high resolution and high development properties cannot be obtained and used as a resist material. Furthermore, the average molecular weight (M_w) is measured using the photo dispersion method. Also, the average molecular number (M_n) is measured using the film permeation pressure method.

[0016] In addition, the average molecular weight of the above described block copolymer is not particularly limited but when it is used as the resist material, in general, the average molecular number is in the range of 500 - 50,000. In particular, this range is most preferred, 3,000 - 300,000. When the average molecular number is below 500, the film strength when used as the resist material is poor. When the average molecular number is above 50,000, the development property and the solubility becomes a problems. High resolution and high development properties cannot be obtained.

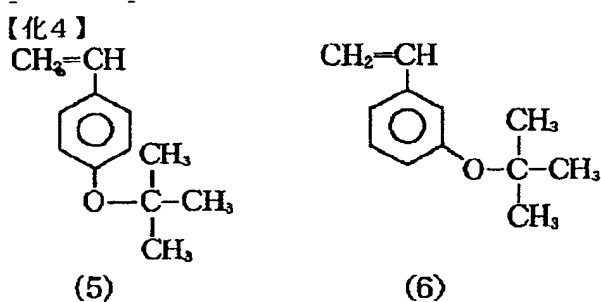
[0017] Furthermore, the evaluation of the above molecular weight distribution can be performed by the Gel Permeation Chromatography (GPC). The molecule structure is obtained easily by ^1H - NMR spectral.

[0018] The partially esterified p - hydroxy styrene - m - hydroxy styrene block copolymer of single dispersion as described above in the invention can be obtained easily by esterified partially the hydroxide group of the p - butoxy styrene - m - hydroxy styrene block copolymer with the dispersion property as described below.

[0019] Here, first, the single dispersed block copolymer of the p - hydroxy styrene and m - hydroxy styrene can be obtained by the living polymerization of the two monomers of the p - t - butoxy styrene shown with the structural formula (5) given below and the m - t - butoxy styrene shown with the structural formula (6) given below, the t - butyl group in the molecule is separated.

[0020]

[Formula 4]



[0021] Also, when the above monomers are living polymerized, it is preferred that an organic metal compound is used as the polymerization initiating agent. The examples of the organic metal compound are the organic alkaline metal such as n - butyl lithium, sec - butyl lithium, t - butyl lithium, sodium naphthalene, anthracene sodium, alpha - methyl styrene tetramer disodium can be used. Furthermore, the addition amount of the polymerization initiating agent depends on the molecular weight of the polymer produced, it is calculated from the weight of the monomer (molecular weight = monomer weight/mole number of initiating agent).

/5

[0022] It is preferred that the living polymerization is performed generally in the organic solvent. The examples of the organic solvent are the aromatic group of hydrocarbon, the ring shaped ether and the aliphatic group of hydrocarbon solvent can be used. The specific examples are such as benzene, toluene, tetrahydrofuran, dioxane, tetrahydropilane, dimethoxy ethane, n - hexane and cyclohexane can be used. It is preferred that 2 or more

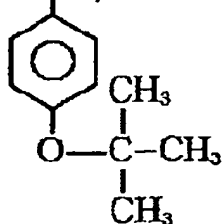
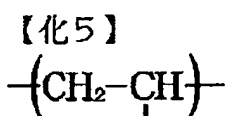
of the above organic solvents are combined together. Furthermore, it is preferred that the concentration in the organic solvent of the two monomer shown in formula (5) & (6) is preferred in 1 - 50 %, it is particularly preferred in this range 1 - 30 %.

[0023] It is preferred that the reaction is carried out under inert gas atmosphere such as nitrogen, argon or in high vacuum. The reaction temperature can be selected freely between the boiling point of the organic solvent used from -100°C but in particular, it is preferred to be reacted in -78°C - 0°C in the tetrahydrofuran solvent but preferably the reaction is carried out at room temperature in the benzene solvent. Also, the reaction is preferred to be carried out in the range of about 10 minutes - 20 hours.

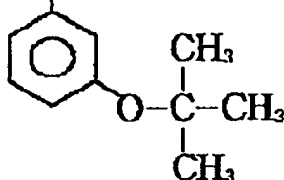
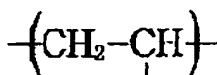
[0024] The stopping of the reaction can be carried out by addition to the reaction system the stopping agent such as methanol, water, methyl bromide, etc. Next, the reaction mixture solution is precipitated in a suitable solvent such as methanol, it is washed, and dried. A polymer produced by polymerization reaction is purified, and single separated. Furthermore, by the living polymerization reaction, only the vinyl group in the monomer of formula (5) and (6) is reacted and polymerized selectively. A block copolymer having the repeated units shown in the structural formula (7) and (8) shown below is obtained.

[0025]

[Formula 5]



(7)



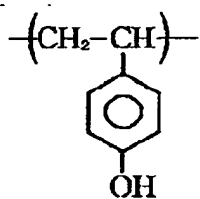
(8)

[0026] The copolymer obtained in this way has a molecular weight distribution of M_w/M_n equal to 1.01 - 1.5 of single dispersion.

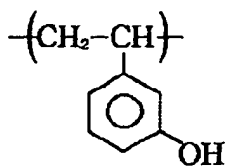
[0027] Furthermore, the yield of the polymer in the above reaction is almost 100 %, the molecular weight of the polymer that is obtained is calculated easily from the mole number (molecule number) of the polymerization initiating agent and the weight of the monomer that is used.

[0028] Next, by separating the t - butyl group in the block copolymer having the repeated units shown with the above formula (7) and (8), the block copolymer of p - hydroxy styrene and the m - hydroxy styrene having phenol remaining group structural unit shown by the formula (9) and (10) given below.

[0029]



(9)



(10)

(10)

[0030] The separation reaction of the above described t - buthyl group can be performed easily by dropping acid such as hydrogen bromide, hydrochloric acid in the solvent mixture or single solvent such as benzene. In these reactions, the main chain of the polymer is cut. Since there is no linking reaction between the molecule, the molecular distribution of the block copolymer of p - t - buthoxy styrene which is the precursor and the m - t - buthoxy styrene can be maintained. The copolymer block of the m - hydroxy styrene and the p - hydroxy styrene of single dispersion of narrow molecular weight distribution is obtained.

[0031] Furthermore, in this case, the addition amount of the acid is added at the same mole as the poly (p - hydroxy styrene) and poly (m - hydroxy styrene)

[0032] In addition, the reaction for partial conversion of the hydroxide group by t - buthoxy carbonyl can be carried out easily similar to the normal t - buthoxy carbonyl reaction, the hydroxide groups are the poly (m - hydroxy styrene) part and the poly (p - hydroxy styrene) part of the copolymer block of m - hydroxy styrene and the p - hydroxy styrene of single dispersion as described above.

[0033] For example, the examples of the t - butoxy carbonyl chemicals are such as chlorogy acid - t - butyl, di - t - butyl carbonate, t - butoxy carbonyl thio - (4, 6 - dimethyl pyridine), t - butyl penta chlorophenyl carbonate, 2 - (t - butoxy carbonyl oxyimino) - 2 - phenyl acetonitrile can be used. Also, the examples of the acid trap solvent is the used of pyridine and tetra ethyl amine. The hydroxide groups of poly (m - hydroxy styrene) part and the poly (p - hydroxy styrene) part of single dispersion are t - butoxy carbonyl converted partially. In this case, this can be added if necessary, for example, dimethyl amine, 4 - N, N - dimethyl amino pyridine is added to the reaction system as the t - butoxy carbonyl catalyst. Furthermore, the usage amount of the t - butoxy carbonyl chemical agent is inversely proportionally to the t - butoxy carbonyl rate. The addition amount of the t - butoxy carbonyl catalyst can be the catalyst amount. In addition, the usage amount of the acid trap solvent have the same mole as the t - butoxy carbonyl chemical agent.

/6

[0034] Also, the block copolymer of p - hydroxy styrene and m - hydroxy styrene is converted into potassium salt using potassium - t - butoxide. The block copolymer of the m - hydroxy styrene and the p - hydroxy styrene of single dispersion can be esterified by t - butoxy carbonyl partially according to the reaction of the di - t - butyl carbonate. Furthermore, the t - butoxy carbonyl reaction in the invention is not limited to the above reaction.

[0035] Since the t - butoxy carbonyl conversion rate of the p -

hydroxy styrene - m - hydroxy styrene copolymer of single dispersion that was esterified partially in the invention as obtained above can be verified easily by the ^1H - NMR spectral, this t - butoxy carbonyl conversion rate is about 0.1 - 80 % to the poly (m - hydroxy styrene) and poly (hydroxy styrene) from the observation point of the cross linking reaction control and the difference in the solubility during the development of the resist as described above, this conversion rate is more preferred at 5 - 45 %.

[0036]

[Effect of Invention] The copolymer block of p - hydroxy styrene - m - hydroxy styrene that is esterified partially with the t - butoxy carbonyl group of the invention can be developed with an alkaline solution and since the molecular weight distribution is narrow, it is suitable as the photosensitive polymer material as the resist material of high resolution. Also, according to the production method of the invention, the block copolymer of p - hydroxy styrene - m - hydroxy styrene of the t - butoxy carbonyl group partially esterified with single dispersion can be produced effectively for the industry since the molecular weight can be controlled easily.

[0037]

[Implementation example] The implementation example is shown below for explaining the invention in detail but the invention is not limited by the implementation example.

[0038] [Implementation example]

The synthesis of the block copolymer of the m - hydroxy styrene and the p - hydroxy styrene of single dispersion

2300 ml of Tetrahydroxy furan used as the solvent and 8×10^{-3} mole of n - butyl lithium used as the initiating agent are introduced into a 3 liter flask. These are mixed and the solution mixture that is obtained is cooled to -78°C . 100 g of p - tert - butoxy styrene is added to this solution. After stirring for 2 hours, the polymerization reaction is carried out. Next, 5 g of m - tert - butoxy styrene is added, the polymerization reaction is carried out while stirring for 2 hours, the reaction solution reaches red color. Next, the polymerization reaction is stopped by adding methanol as the reaction stopping agent in the reaction solution that is obtained. Then, this solution is poured into the methanol, the polymer obtained is precipitated, it is dried centrifugally, then a white polymer of 104 g is obtained.

[0039] The measurement results from the 1H - NMR of the polymer that is obtained are given below:

1.4 - 2.2 ppm : (broad, 3H, $-\text{CH}_2-\text{CH}-$)

1.3 - 1.6 ppm : (broad, 9H, $-\text{OC}(\text{CH}_3)_3$)

6 - 7 ppm: (broad, 4H, C_6H_4)

[0040] From the 1H -NMR computation results, it is verified that the copolymer obtained from above is the copolymer consists of 95 % of p - tert - butoxy styrene and 5 % of m - tert - butoxy styrene. Also, the average molecular number if measured by the film permeation pressure measurement method, it is 1.2×10^4 g/mole. In addition, from the GPC elution curve, it is verified that the

single dispersion rate is extremely high ($M_w/M_n = 1.09$). Furthermore, the GPC elution curve is according to the figure 1.

[0041] Next, after the above obtained copolymer of 20 g is dissolved by adding to 300 ml of acetone. The solution that is obtained is stirred for 8 hours, then, this solution is poured into water, it is washed and dried, 13 g of polymer is obtained.

[0042] The average molecular number of the polymer is measured according to the film permeation pressure measurement method, 7600 g/mole is obtained. Also, the molecular weight distribution of this polymer is according to figure 2 from the result obtained by GPC. It is verified that the copolymer have extremely high single dispersion rate. In addition, from the measurement results of 1H -NMR of the polymer that is obtained, since there is no original peak in the tert - butyl group, the polymer is the copolymer of poly (p - hydroxy styrene) and poly (m - hydroxy styrene), it does not have the tert - butyl group.

[0043] Synthesis of the block copolymer of p - hydroxy styrene and m - hydroxy styrene that is partially esterified with tert - butoxy carbonyl group.

100 g of block copolymer (molecular weight of 7600 and molecular weight distribution of 1.15) of p - hydroxy styrene and m - hydroxy styrene obtained from the above living polymerization is dissolved in 1 liter of pyridine. 40 g of di - t - butyl dicarbonate is added while stirring the solution at 45°C. Gas is generated at the same time of the addition. In addition, it is reacted temporarily in N_2 gas. The reaction solution is dropped into 1 liter of water

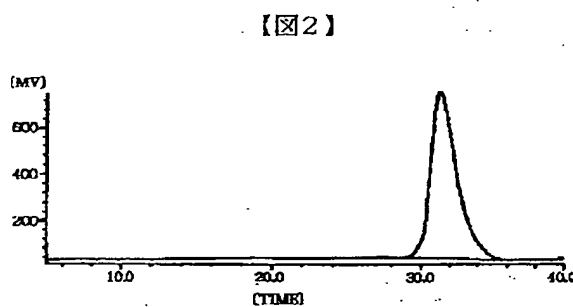
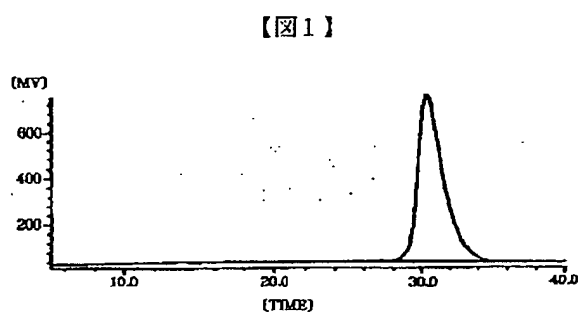
containing a concentrated acid of 20 g. A white precipitate is obtained. After filtering, it is precipitated and dissolved in 50 ml of acetone and then dropped into 1 liter of water. Next, the precipitation is filtered and vacuum dry below 40°C.

[0044] The polymer obtained have the repeated units of the aforementioned formula (1), (2), (3) and (4). The introduction rate of the tert - butoxy carbonyl group using the peak OH group of 8 ppm is 19.6 % in the ^1H - NMR. Also, the molecular weight distribution is 1.15.

[Brief explanation of the diagrams]

[Figure 1] This is the graph showing the GPC elution curve of the block copolymer of the m - tert - butoxy styrene and p - tert - butoxy styrene obtained in the implementation example.

[Figure 2] This is the graph showing the GPC elution curve of the block copolymer of the m - hydroxy styrene and p - hydroxy styrene obtained in the implementation example.



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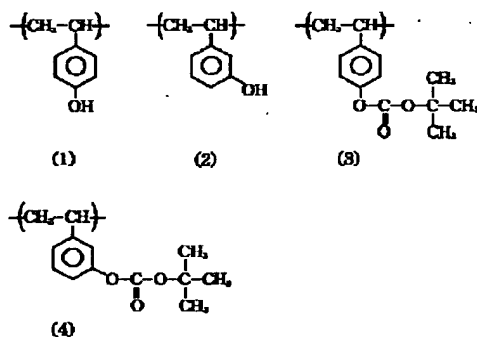
(54)【発明の名称】 tert-ブトキシカルボニル基で部分エステル化されたp-ヒドロキシスチレン-m-ヒドロキシスチレンブロック共重合体及びその製造方法

(57)【要約】

【目的】 アルカリで容易に現像することができると共に、単分散性で高現像性及び高解像度を有し、機能性高分子としてレジスト材料等の用途に好適なポリマーを提供する。

【構成】 重量平均分子量(M_w)／数平均分子量(M_n)が1.01～1.5の単分散性のp-ヒドロキシスチレンとm-ヒドロキシスチレンとのブロック共重合体中のポリ(p-ヒドロキシスチレン)部及びポリ(m-ヒドロキシスチレン)部の水酸基を部分的にtert-ブトキシカルボニル化して、下記構造式(1)、(2)、(3)及び(4)で示される繰り返し単位を有し、かつ分子量分布が重量平均分子量(M_w)／数平均分子量(M_n)=1.01～1.5であるポリ(p-ヒドロキシスチレン)部及びポリ(m-ヒドロキシスチレン)部の水酸基がtert-ブトキシカルボニル基で部分エステル化されたp-ヒドロキシスチレン-m-ヒドロキシスチレンブロック共重合体を得る。

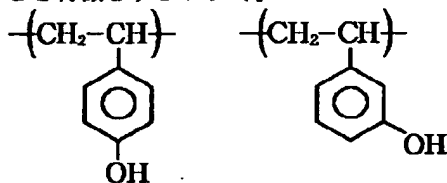
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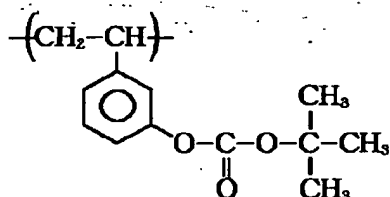
【特許請求の範囲】

【請求項1】 下記構造式(1)、(2)、(3)及び(4)で示される繰り返し単位を有し、かつ分子量分布が重量平均分子量(M_w)/数平均分子量(M_n)=1.01~1.5であることを特徴とするポリ(p-ヒドロキ



(1)

(2)



(4)

【請求項2】 重量平均分子量(M_w)/数平均分子量(M_n)が1.01~1.5の単分散性のp-ヒドロキシスチレンとm-ヒドロキシスチレンとのブロック共重合体中のポリ(p-ヒドロキシスチレン)部及びポリ(m-ヒドロキシスチレン)部の水酸基を部分的にtert-ブトキシカルボニル化する請求項1記載のp-ヒドロキシスチレン-m-ヒドロキシスチレンブロック共重合体の製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明はLSI用のレジスト材等として好適に用いられるポリ(p-ヒドロキシスチレン)部及びポリ(m-ヒドロキシスチレン)部の水酸基がtert-ブトキシカルボニル基で部分エステル化された単分散性のp-ヒドロキシスチレン-m-ヒドロキシスチレンブロック共重合体及びその製造方法に関する。

【0002】

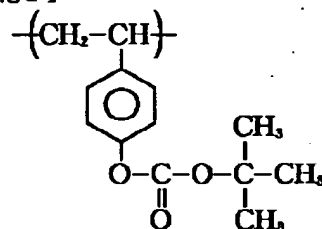
【従来の技術及び発明が解決しようとする課題】従来、高解像度のリソグラフィー用、或いはLSI用として使用するレジスト材料用ベースポリマーとしては、機能性高分子が多用されている。特に近年のLSIにおける高密度化の進展に伴い、レジスト材料については益々高解像度及び高現像性が要求されるようになり、このような要求に応え得る機能性高分子として従来はノボラック樹脂が主流に使用されていたが、最近においてはこれに代わるものとして化学増幅タイプのレジスト材料が種々検討されている。

【0003】上記化学増幅タイプのレジスト材料におい

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*キシスチレン)部及びポリ(m-ヒドロキシスチレン)部の水酸基がtert-ブトキシカルボニル基で部分エステル化されたp-ヒドロキシスチレン-m-ヒドロキシスチレンブロック共重合体。

【化1】



(3)

※ては、特に作業性の観点から酸によって容易に脱離する官能基を有すると共に、その官能基の脱離前後での溶解性が異なるものが賞用されている。このようなレジスト材料としては耐プラズマ性に優れているポリスチレン誘導体が特に好適なものとして知られている。

【0004】これらのポリマーをレジスト用ベースポリマーとして使用する場合には、その分子量や分子量分布がレジストの現像特性及び解像度に大きな影響を与えるが、これらのポリマーは通常のラジカル重合法や縮重合法により得られる多分散ポリマーであって、はじめから分子量や分子量分布を制御することが配慮されていないので、レジストの現像性及び解像度を高めるため、分別という手法を用いて分子量の制御を行っている。

【0005】しかしながら、分別という手法は操作が複雑であるのみならず時間がかかるという欠点がある上、厳しくなる要求性能に対して十分に追従することが困難であるので、問題解決の本質的手段にはなり得ないものであった。

【0006】従って、レジスト材料用ベースポリマーとして好適な高品質のポリマーの開発が望まれていた。

【0007】本発明は上記要望に応えるためなされたもので、酸によって容易に脱離する官能基を有するので、その官能基の脱離前後での溶解性が異なることでアルカリで容易に現像することができると共に、高現像性及び高解像度を有し、レジスト材料等として有用なポリ(p-ヒドロキシスチレン)部及びポリ(m-ヒドロキシスチレン)部の水酸基がtert-ブトキシカルボニル基で部分エステル化されたp-ヒドロキシスチレン-m-

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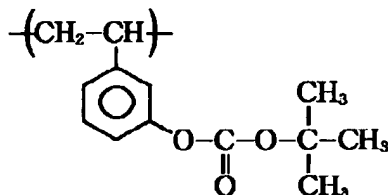
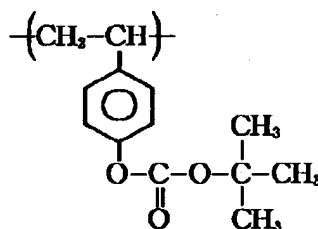
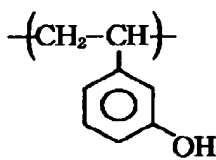
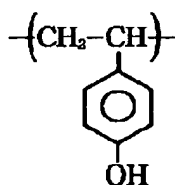
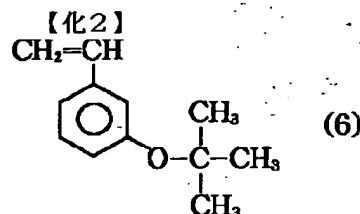
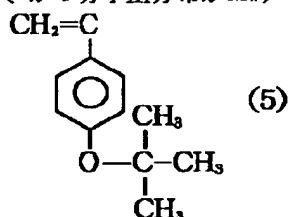
3

ヒドロキシスチレンブロック共重合体及びその製造方法を提供することを目的とする。

【0008】

【課題を解決するための手段及び作用】本発明者は上記目的を達成するため鋭意検討を重ねた結果、下記構造式(5)で示されるp-tert-ブトキシスチレンと下記構造式(6)で示されるm-tert-ブトキシスチレンとをリビング重合させた後、分子中のtert-ブチル基を脱離させることにより、重量平均分子量

(M_w)/数平均分子量(M_n)が1.01~1.5の単分散性のp-ヒドロキシスチレンとm-ヒドロキシスチレンとのブロック共重合体を得られること、そして該ブロック共重合体中のポリ(p-ヒドロキシスチレン)部及びポリ(m-ヒドロキシスチレン)部の水酸基を部分的にtert-ブトキシカルボニル化することにより、下記構造式(1)、(2)、(3)及び(4)で示される繰り返し単位を有し、かつ分子量分布が $M_w/M_n =$ *



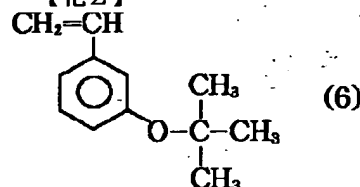
【0010】従って、本発明は、上記構造式(1)、(2)、(3)及び(4)で示される繰り返し単位を有し、かつ分子量分布が重量平均分子量(M_w)/数平均分子量(M_n)=1.01~1.5であることを特徴とするポリ(p-ヒドロキシスチレン)部及びポリ(m-ヒドロキシスチレン)部の水酸基がtert-ブトキシカルボニル基で部分エステル化されたp-ヒドロキシスチレン-m-ヒドロキシスチレンブロック共重合体、及び重量平均分子量(M_w)/数平均分子量(M_n)が1. ※50

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* 1.01~1.5であるポリ(p-ヒドロキシスチレン)部及びポリ(m-ヒドロキシスチレン)部の水酸基がそれぞれtert-ブトキシカルボニル基で部分エステル化されたp-ヒドロキシスチレンとm-ヒドロキシスチレンとのブロック共重合体を得られること、この方法は分子量の制御が容易であり、かつ確実に $M_w/M_n = 1.01~1.5$ の単分散性のブロック共重合体を与えるものであると共に、このようにして得られた単分散性ブロック共重合体が酸によって容易に脱離し得るtert-ブトキシカルボニル基を有し、アルカリで容易に現像することができる上、単分散性で分別という面倒な手法を行わなくても高現像性及び高解像度を有し、それ故、機能性高分子としてレジスト材料用ベースポリマー等の用途に好適に利用できることを知見し、本発明をなすに至った。

【0009】

【化2】



※01~1.5の単分散性のp-ヒドロキシスチレンとm-ヒドロキシスチレンとのブロック共重合体中のポリ(p-ヒドロキシスチレン)部及びポリ(m-ヒドロキシスチレン)部の水酸基を部分的にtert-ブトキシカルボニル化する上記部分エステル化されたp-ヒドロキシスチレン-m-ヒドロキシスチレンとのブロック共重合体の製造方法を提供する。

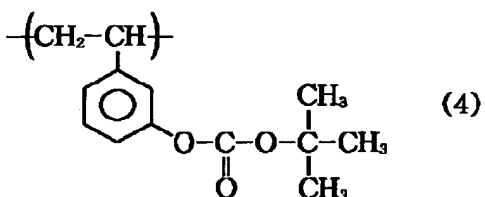
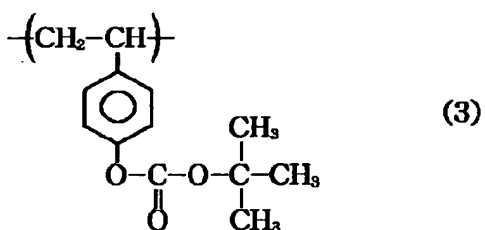
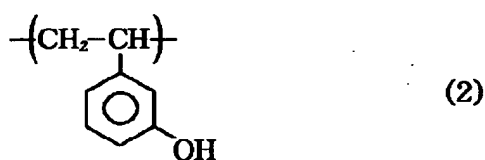
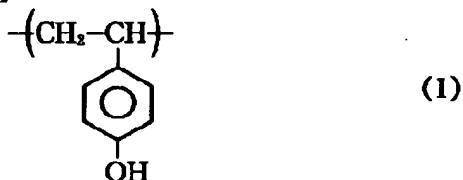
【0011】以下、本発明につき更に詳述すると、本発明のブロック共重合体は、下記構造式(1)、(2)、

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(3) 及び (4) で示される繰り返し単位を有するポリ(p-ヒドロキシスチレン)部及びポリ(m-ヒドロキシスチレン)部の水酸基がtert-ブトキシカルボニル基で部分エステル化されたものである。

【0012】

【化3】



【0013】ここで、上記式(1)、(2)、(3)及び(4)の繰り返し単位は任意の割合で含有してよいが、通常は重量分率が $0.01 \leq (1) \leq 99.97$ 、 $0.01 \leq (2) \leq 99.97$ 、 $0.01 \leq (3) \leq 99.97$ 、 $0.01 \leq (4) \leq 99.97$ 、 $(1) + (2) + (3) + (4) = 1$ となるような割合で含有することが好ましく、特に本発明のブロック共重合体をレジスト材として使用する場合は、レジストの現像時における溶解性の差及び架橋反応制御の観点から $20 \leq (1) \leq 99.98$ 、 $0.01 \leq (2) \leq 50$ 、 $0.01 \leq (3) \leq 80$ 、 $0.01 \leq (4) \leq 50$ 、より好ましくは $50 \leq (1) \leq 99.8$ 、 $0.01 \leq (2) \leq 20$ 、 $0.01 \leq (3) \leq 45$ 、 $0.01 \leq (4) \leq 20$ とすることが好適である。

【0014】更に、上記ブロック共重合体において分子中の水酸基のtert-ブトキシカルボニル基による部分エステル化の割合は、ポリ(p、m-ヒドロキシスチレン)に対して0.1~80% (重量%、以下同様)、特に5~45%であることが好ましい。

6

【0015】本発明の上記p-ヒドロキシスチレンとm-ヒドロキシスチレンとのブロック共重合体は、 M_w/M_n が1.01~1.5、好ましくは1.01~1.3の範囲となるような分子量分布を有する単分散性のものである。 M_w/M_n が1.01に満たないものは技術的に合成困難であり、1.5を超えるとレジスト材料として利用できる程度の高解像度、高現像度を得ることができない。なお、重量平均分子量(M_w)は光散乱法により、また、数平均分子量(M_n)は膜浸透圧計を用いて測定することができる。

【0016】更に、上記ブロック共重合体の平均分子量は特に制限されるものではないが、レジスト材料として使用する場合は、一般に数平均分子量が500~500,000の範囲、特に3,000~300,000の範囲であることが好ましい。数平均分子量が500未満ではレジスト材料として膜強度が無い場合があり、500,000を超えると現像特性、相溶性に問題があり、高解像度、高現像度を得ることができない場合がある。

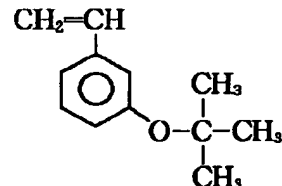
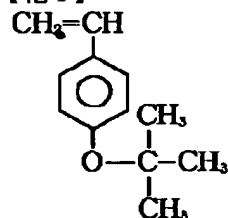
【0017】なお、上記分子量分布の評価はゲルパーミエーションクロマトグラフィー(GPC)によって行うことができ、分子構造は $^1\text{H-NMR}$ スペクトルによって容易に確認することができる。

【0018】本発明において上述した単分散性の部分エステル化p-ヒドロキシスチレン-m-ヒドロキシスチレンブロック共重合体は、以下に示す如く単分散性p-ヒドロキシスチレン-m-ヒドロキシスチレンブロック共重合体の水酸基をtert-ブトキシカルボニル基によって部分的にエステル化することにより容易に得ることができる。

【0019】ここでまず、単分散性のp-ヒドロキシスチレンとm-ヒドロキシスチレンのブロック共重合体は、下記構造式(5)で示されるp-tert-ブトキシスチレンと下記構造式(6)で示されるm-tert-ブトキシスチレンの両モノマーをリビング重合させた後、分子中のtert-ブチル基を脱離することによって得ることができる。

【0020】

【化4】



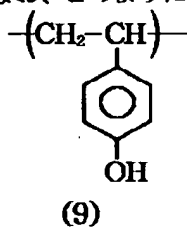
【0021】また、上記モノマーのリビング重合に際しては、重合開始剤として有機金属化合物を用いることが好ましい。有機金属化合物としては、例えばn-ブチルリチウム、sec-ブチルリチウム、tert-ブチルリチウム

ム、ナトリウムナフタレン、アントラセンナトリウム、 α -メチルスチレンテトラマーナトリウム、クミルカリウム、クミルセシウム等の有機アルカリ金属などが挙げられる。なお重合開始剤の添加量は、生成するポリマーの分子量に依存しており、分子量とモノマーの重量から算出される(分子量=モノマーの重量/開始剤のモル数)。

【0022】リビング重合は一般に有機溶媒中で行うことが望ましい。有機溶媒としては芳香族炭化水素、環状エーテル、脂肪族炭化水素溶媒等が例示され、具体例としてベンゼン、トルエン、テトラヒドロフラン、ジオキサン、テトラヒドロピラン、ジメトキシエタン、 n -ヘキサン、シクロヘキサン等が挙げられる。これらの有機溶媒はそれぞれ単独で使用しても2種以上を組み合わせ使用してもよい。なお、上記両モノマー式(5)、(6)の有機溶媒中の濃度は、1~50%、特に1~30%とすることが好ましい。

【0023】反応は高真空下又はアルゴン、窒素等の不活性ガス雰囲気下で撹拌して行うことが好ましい。反応温度は-100℃から使用した有機溶媒の沸点温度までの間で自由に選択することができるが、特にテトラヒドロフラン溶媒では-78℃~0℃、ベンゼン溶媒では室温で反応させることが好ましい。また、反応は通常約10分~20時間行うことが好適である。

【0024】反応の停止は、例えばメタノール、水、メチルプロマイド等の停止剤を反応系に添加することによって行う。次いで、得られた反応混合溶液を適当な溶剤、例えばメタノール中に沈澱せしめ、洗浄、乾燥することにより、重合反応によって生成したポリマーを精製、単離することができる。なお、このようにリビング*



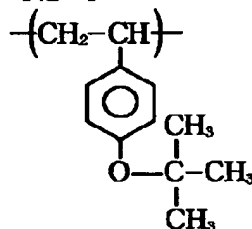
【0030】上記の α -ブチル基の脱離反応は、ジオキサン、アセトン、アセトニトリル、ベンゼン等の単独又は混合溶媒中で塩酸、臭化水素酸等の酸を滴下することによって容易に行うことができる。これらの反応においては、高分子の主鎖が切断されたり、分子間に架橋反応が起こるといったことがないので、前駆体である p - α -ブトキシスチレンと m - α -ブトキシスチレンとのブロック共重合体の分子量分布がそのまま維持されて、分子量分布の狭い単分散の p -ヒドロキシスチレンと m -ヒドロキシスチレンとのブロック共重合体を得ることができる。

【0031】なおこの場合、酸の添加量はポリ(p -ヒドロキシスチレン)とポリ(m -ヒドロキシスチレン)※50

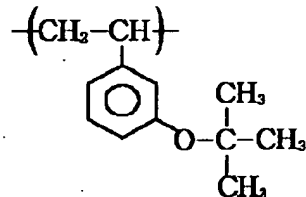
*重合反応を行うと、上記式(5)及び(6)のモノマー中のビニル基のみが選択的に反応して重合し、下記構造式(7)及び(8)で示される繰返し単位を有するブロック共重合体を得られる。

【0025】

【化5】



(7)



(8)

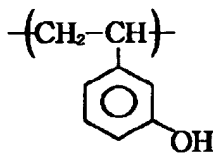
【0026】このようにして得られる共重合体は、分子量分布 M_w/M_n が1.01~1.5の単分散性のものである。

【0027】なお、上記反応におけるポリマーの収率はほぼ100%であるので、得られるポリマーの分子量は使用したモノマーの重量と重合開始剤のモル数(分子数)から容易に算出できる。

【0028】次に、上記式(7)及び(8)で示される繰返し単位を有するブロック共重合体中の α -ブチル基を脱離させるとことにより、下記構造式(9)及び(10)で示されるフェノール残基構造単位を有する p -ヒドロキシスチレンと m -ヒドロキシスチレンとのブロック共重合体を得られる。

【0029】

【化6】



(10)

※と等モル以上添加すればよい。

【0032】更に、上述の単分散の p -ヒドロキシスチレンと m -ヒドロキシスチレンとのブロック共重合体のポリ(p -ヒドロキシスチレン)部及びポリ(m -ヒドロキシスチレン)部の水酸基を部分的に α -ブトキシカルボニル化する反応は、通常の α -ブトキシカルボニル化反応と同様にして容易に行うことができる。

【0033】例えば、 α -ブトキシカルボニル化試薬として、クロロギ酸- α -ブチル、ジ- α -ブチルカーボネート、 α -ブトキシカルボニルチオール(4,6-ジメチルピリジン)、 α -ブチルペンタクロロフェニルカーボネート、2-(α -ブトキシカルボニルオキシイミノ)-2-フェニルアセトニトリル等を使用し、かつ酸

トラップ溶媒としてピリジン、テトラエチルアミン等を用いて、単分散のポリ(p-ヒドロキシスチレン)部及びポリ(m-ヒドロキシスチレン)部の水酸基を部分的にt-ブトキシカルボニル化する。この場合、必要に応じてジメチルアミン、4-N, N-ジメチルアミノピリジン等をt-ブトキシカルボニル化触媒として反応系に添加してもよい。なお、t-ブトキシカルボニル化試薬の使用量は、t-ブトキシカルボニル化率に比例量であり、t-ブトキシカルボニル化触媒の添加量は触媒量とすることができる。更に酸トラップ溶媒の使用量は、t-ブトキシカルボニル化試薬と等モルが好適である。

【0034】また、カリウム-t-ブトキシドを用いてp-ヒドロキシスチレンとm-ヒドロキシスチレンとのブロック共重合体をカリウム塩にし、これをジ-t-ブチルジカーボネートと反応させる方法によっても単分散のp-ヒドロキシスチレンとm-ヒドロキシスチレンとのブロック共重合体を部分的にt-ブトキシカルボニル化することができる。なお、本発明におけるt-ブトキシカルボニル化反応は上記反応に限定されるものではない。

【0035】このようにして得られる本発明の部分エステル化単分散性p-ヒドロキシスチレン-m-ヒドロキシスチレン共重合体のt-ブトキシカルボニル化率は、¹H-NMRスペクトルによって容易に確認することができるもので、このt-ブトキシカルボニル化率は、上述したようにレジストの現像時における溶解性の差及び架橋反応制御の観点からポリ(p-ヒドロキシスチレン)とポリ(m-ヒドロキシスチレン)に対してそれぞれ0.1~80%、特に5~45%の範囲であることが好ましい。

【0036】

【発明の効果】本発明のt-ブトキシカルボニル基で部分エステル化されたp-ヒドロキシスチレン-m-ヒドロキシスチレンブロック共重合体は、アルカリ現像でき、かつ分子量分布が狭いので、高解像度のレジスト材料等の感光性高分子材料として好適である。また、本発明の製造方法によれば、上記単分散性のt-ブトキシカルボニル基部分エステルのp-ヒドロキシスチレン-m-ヒドロキシスチレンとのブロック共重合体をその分子量を任意にかつ容易に制御して工業的に有利に製造することができる。

【0037】

【実施例】以下、実施例を示し、本発明を更に詳述するが、本発明はこれによって限定されるものではない。

【0038】〔実施例〕

単分散性のp-ヒドロキシスチレンとm-ヒドロキシスチレンとのブロック共重合体の合成

3リットルのフラスコに溶媒としてテトラヒドロフラン2300ml、開始剤としてn-ブチルリチウム8×10⁻³モルを仕込み、混合した。得られた混合溶液を-7

8℃に冷却した後、この溶液にp-tert-ブトキシスチレン100gを添加し、2時間攪拌しながら重合反応を行わせ、次にm-tert-ブトキシスチレン5gを添加し、2時間攪拌しながら重合反応を行わせたところ、反応溶液は赤色を呈した。次いで、得られた反応溶液に反応停止剤としてメタノールを添加して重合反応を停止させた後、この溶液をメタノール中に注ぎ、得られた重合体を沈澱させ、分離乾燥させたところ、白色の重合体104gが得られた。

10 【0039】得られた重合体の¹H-NMRの測定結果は下記の通りである。

1. 4~2.2ppm: (ブロード, 3H, -CH₂-CH-)

1. 3~1.6ppm: (ブロード, 9H, -OC(C₂H₅)₃)

6~7ppm: (ブロード, 4H, C₆H₄)

【0040】¹H-NMR測定結果から、上記の共重合体は、p-tert-ブトキシスチレン95%及びm-tert-ブトキシスチレン5%からなる共重合体であることが確認された。また、膜浸透圧測定法によって数平均分子量を測定したところ、1.2×10⁴g/モルであった。更に、GPC溶出曲線の結果から、単分散性が極めて高い(M_w/M_n=1.09)ことが確認された。なお、GPC溶出曲線は図1に示した通りである。

【0041】次いで、上記共重合体20gをアセトン300mlに加えて溶解させた後、60℃で少量の濃塩酸を添加した。得られた溶液を8時間攪拌した後、この溶液を水中に注ぎ、洗浄・乾燥させたところ、ポリマー13gが得られた。

30 【0042】膜浸透圧測定法によりこのポリマーの数平均分子量を測定したところ7600g/モルであった。また、このポリマーの分子量分布をGPCにより評価した結果は図2に示した通りであり、極めて単分散性の高い共重合体であることが確認された。更に、ここで得られたポリマーの¹H-NMRの測定結果からtert-ブチル基に由来するピークが観測されなかったため、ポリマーがポリ(p-ヒドロキシスチレン)とポリ(m-ヒドロキシスチレン)との共重合体であって、tert-ブチル基を全く有していないことが確認された。

40 【0043】tert-ブトキシカルボニル基で部分エステル化されたp-ヒドロキシスチレンとm-ヒドロキシスチレンとのブロック共重合体の合成

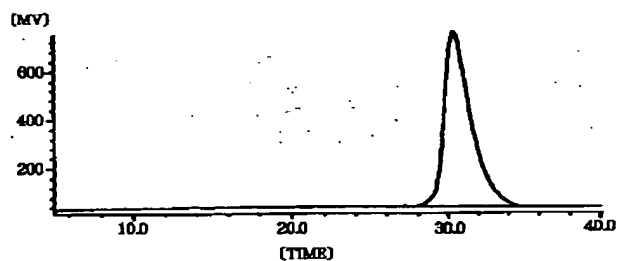
上記リビング重合で得られたp-ヒドロキシスチレンとm-ヒドロキシスチレンとのブロック共重合体(分子量7600、分子量分布1.15)100gをピリジン1リットルに溶解させ、45℃で攪拌しながら二炭酸ジ-t-ブチルを40g添加した。添加と同時にガスが発生したが、更にN₂気流中で一時間反応させた。濃塩酸20gを含む水1リットルに反応液を滴下し、白色の沈澱を得た。ろ過した後、アセトン50mlに沈澱溶解さ

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せ、水1リットルに滴下した。次いで、沈澱をろ過した後、40℃以下で真空乾燥した。

【0044】得られたポリマーは前記式(1)、(2)、(3)及び(4)の繰り返し単位を有するもので、 $^1\text{H-NMR}$ における8ppmのOH基のピークを用いてtert-ブトキシカルボニル基の導入率を求めた結果、19.6%であり、また分子量分布は1.15であった。

【図1】



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【図面の簡単な説明】

【図1】実施例で得られたp-tert-ブトキシスチレンとm-tert-ブトキシスチレンとのブロック共重合体のGPC溶出曲線を示すグラフである。

【図2】実施例で得られたp-ヒドロキシスチレンとm-ヒドロキシスチレンとのブロック共重合体のGPC溶出曲線を示すグラフである。

【図2】

